STRUCTURE OF COALS REVEALED BY SLOW STEP SCAN XRD AT THEIR SWELLING

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ABSTRACT

Argonne coal samples were treated in dilute acetic acid aq. or polar solvents such as DMF and pyridine, and analyzed by high resolution slow step scan XRD to clarify the effects of such pretreatments on the secondary aggregate structure in the coals caused by non-covalent bonds interactions. Solvent swelling ratios of the lower ranked Beulah-Zap and Wyodak coals with pyridine and DMF increased significantly by the mild acid treatment, suggesting that the coal aggregate structure may be rearranged to more mobile and weaker forms through the removal of ion-exchangeable cations. The slow step scan XRD profiles of the coals showed that the peaks for the organic components can be classified into two parts; one is ascribed to the aromatic plane stacking interactions (around 26 °), the other is probably due to the interactions among aliphatic side chains (around 20 °, that is called γ-band). The solvent-swollen coals with polar solvents such as pyridine or DMF intensified the peaks for the γ-band even after the removal of the solvent by washing with methanol. The solvent-impregnated coal gel (solvent/coal weight ratio of unity) also showed the intensified γ-band, suggesting that the solvent itself may contribute to the rearrangement of the ordered packing in the coal aggregate structure probably due to the aliphatic side chain entanglement and hydrogen bond.

INTRODUCTION

Coals consist of primary macromolecular structure and its secondary network, latter of which is caused by aromatic ring stacking, aliphatic side chain entanglement, and hydrogen bonds, cation bridges, charge transfer interactions through oxygen functional groups.[1-5]

Coal pretreatments have been developed to modify the coals for their easier transportation, grinding, drying, storage and the following conversion processes such as pyrolysis, liquefaction, and gasification.[6-9] Flotation and washing treatments with water, acid or basic solution are one of the conventional procedures for the removal of mineral matters and contaminants by a simple gravimetric separation and filtration, respectively. The former process can be performed to the demineralization of coals by the aid of oil agglomeration or air-bubble flotation. The selected solvents for the latter procedure can dissolve a part of water-soluble mineral matters and ion-exchangeable cations during the storage, transportation or grinding procedures.

Solvent swelling and impregnation treatments of the coals have been the one of the most classical methods for the modification of the coal macromolecular structure induced by the non-covalent bonds interactions such as hydrogen bond, electrostatic interactions, and aromatic plane stacking.[10-15] Selection of solvent and its amount required for the swelling or impregnation should be carefully optimized for the design of the most efficient and adequate solvation of the coals. Polar solvents such as pyridine, THF, and DMF have been reputed to be quite effective for the liberation of the non-covalent bonds interactions in the coal macromolecular network. It was reported that the impregnation of a small amount of pyridine enhanced the coal fusibility and the following carbonization reactivity even after the extraction of the soluble fraction, because pyridine played an important role in the liberation of hydrogen bond and the favorable rearrangement of the coal aggregate structure during the heat treatment and carbonization.[16]

X-ray diffraction(XRD) have been applied to the characterization of carbonaceous materials including coals for the better understanding of their molecular-level structuring and ordered packing extent of their unit structure.[17-21] Slow step scan XRD analyses have been reputed to give the higher resolution of the diffractograms, classifying the carbon-related peak around 20 - 26 ° into two parts ; one is derived from aromatic ring stacking around 26 °, and the other is derived from aliphatic chain entanglement around 20 °. The ratio of the two peaks depends on the coal rank, and hence the secondary macromolecular network in coals is influenced by their ratio.

In the present study, four coals in the Argonne Premium Coal Bank were treated in diluted acetic acid or polar solvents such as DMF and pyridine for the modification of the secondary aggregate structure of the coals. A preliminary measurement of the slow step scan XRD indicated that the XRD patterns of the coals may change by the mild acid treatment and/or solvent swelling treatment.[22]

EXPERIMENTAL

Coals

Four coals (100 mesh under) of Beulah-Zap(BZ), Wyodak(WY), Illinois No.6(IL), and Upper Freeport (UF) in the Argonne Premium Coal Bank were used in the present study.

Acid Pretreatment

1.5 g of the coal was treated in aqueous 1.6 mol acetic acid or methoxyethoxy-acetic acid with 10wt% ethanol at room temperature under atmospheric nitrogen flow for 26 - 46 h. After the filtration, the acid-treated coals were dried overnight at 60 °C under vacuum. The filtrates were analyzed by Inductively Coupled Plasma(ICP; SP1500, Seiko Electronics) to quantify the eluted metal cations by the acid treatment. The degrees of the demineralization were calculated based on the difference in the elemental compositions between original and treated coals. The removal ratio of respective metal was calculated based on the ash analysis data supplied from Argonne Premium Coal Bank.

Solvent Swelling and Impregnation

0.4 g of the coal was mixed with a prescribed amount of solvent in a graduated test tube, and settled at 40 °C under nitrogen flow for a few days to measure the swelling ratio by some solvents. Pyridine, DMF, methanol and benzene were used as solvents for the swelling of coal. The swelling ratio (Q) was calculated as follows;

$Q = h_t/h_o$

h_t: height of swollen coal layer in the tube

h_o: height of coal particle layer without solvent

The solvent impregnation treatment of the coals with pyridine, DMF, or THF was performed by mixing the coal powder with solvent at the weight ratio of unity at 40 °C. The solvent-swollen coal was washed with methanol to remove the solvent.

XRD Measurements

The slow step scanning XRD (Rigaku Geigerflex) of coals before and after the acid pretreatments was measured by the scanning speed of 0.4 sec/0.01° at room temperature. The solvent-colas were analyzed by the step scan XRD with or without the removal of solvent.

RESULTS AND DISCUSSION.

Change of Coal Aggregate Structure by the Acid Pretreatment

Figure 1 illustrates slow step scan XRD patterns obtained for coals before and after the acid treatment. In all coals, a broad diffraction profile was obtained around 20 °. The acid treatment intensifies the diffraction in lower-ranked coals of BZ and WY coal. In contrast, a higher-ranked coal of IL did not change its diffraction patterns before and after the acid treatment. It is suggested that ordered packing in the lower ranking coals can be rearranged by the liberation of aggregate structure due to the removal of cation bridge.

Solvent Swelling Behaviors of the Coals

Figure 2 illustrates the swelling ratio in coals of different ranks by four solvents. The extent of swelling of original coal was in the order of pyridine > DMF > methanol > benzene. The acid treatment significantly increased the swelling ratio of the lower rank coals of BZ and WY, while the swelling ratio of IL coal did not change so much by the acid treatment.

Non-treated lower-ranking coals are very refractory against the swelling by the polar solvents such as pyridine and DMF probably due to the strong cation-bridging through the oxygen functional groups. The aggregate structure of a higher-ranked coal IL, is essentially not changed by the acid treatment because of its lower contents of both ion-exchangeable cations and oxygen functional groups, resulting in the insensitivity to the swelling with polar solvents. Less and non-polar solvents showed much smaller swelling of which extent appears rather independent on their ranks.

Figure 3 shows the XRD profiles of BZ coal before and after the solvent swelling treatment with DMF or pyridine followed by washing with methanol. The peak around 20 ° was intensified by the solvent treatment even after the washing with methanol, indicating that solvent swelling treatment with polar solvents may rearrange the aggregate structure caused by aliphatic chain entanglement to more oriented form. It is noted that such effect with DMF is more significant than that with pyridine.

Figure 4 illustrates the XRD profiles of DMF-treated BZ coal before and after the acid treatment. The acid treatment slightly intensified the peak around 26 °, indicating that the aromatic ring stacking may be rearranged to a small extent by the removal of bridging cations. In other words, the solvent treatment of BZ coal with DMF may contribute to the aliphatic chain entanglement, while the acid treatment may be more sensitive to the aromatic ring stacking caused by newly formed hydrogen bonds.

Figure 5 shows the XRD patterns of Beulah-Zap and Wyodak coals before and after the solvent-swelling treatments with and without the removal of DMF. The solvent-swollen coals with polar solvents such as pyridine and DMF intensified the peaks for the γ-band even after the removal of the solvent by washing with methanol. It is noted that the solvent-impregnated coal gel (solvent/coal weight ratio of unity) also showed the intensified γ-band peak without the removal of solvent, suggesting some contribution of the solvent itself to the rearrangement of the coal aggregate structure. It is also suggested that the interaction of polar solvent with coal macromolecules through the oxygen functional groups may survive and influence the secondary aggregate structure in the lower ranked coals even after the removal of solvent.

Figure 6 shows the XRD profiles of IL and UF coals before and after the impregnation treatment with DMF. The DMF-impregnated coals of the higher rank gave a intensified peak around 20 °, although the extent was much smaller than that with the lower ranked coals of BZ and WY. It is suggested that DMF may interact more weakly with the higher ranked coals which have less oxygen functional groups but with more and larger aromatic rings.

Based on the above results, the interactions between coal and solvent can be controlled by changing the combinations of coals of different rank with solvents of different polarity. The slow step scan XRD measurements is effective for the detection of the change in coal aggregate structure caused by the non-covalent bonds interactions such as aliphatic chain entanglement, aromatic ring stacking, charge transfer, and/or hydrogen bonds.

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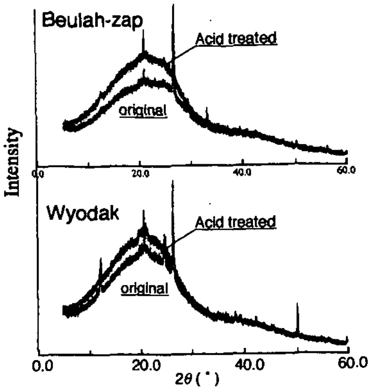

Figure 1 Effect of acid treatment on XRD patterns of BZ and WY coals

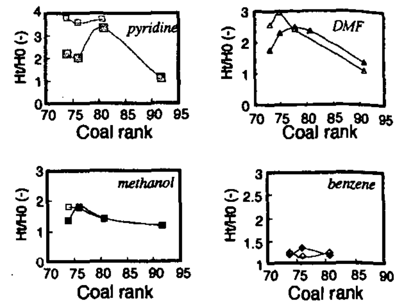

Figure 2 Swelling behavior of coals with various solvents

Opened symbol is acid treated coal
Closed symbol is original coal

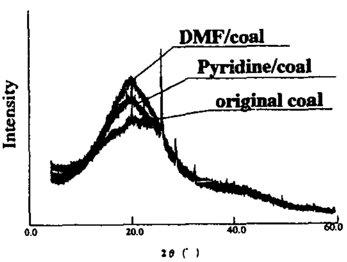

Figure 3 Effects of swelling by DMF and pyridine on XRD patterns of BZ coal with MeOH washing

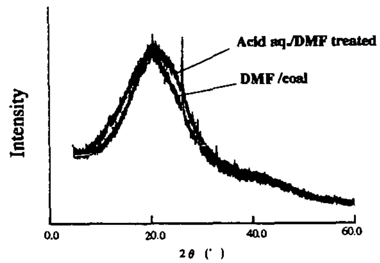

Figure 4 Effect of acid treatment on XRD of DMF-treated BZ-coal with MeOH washing

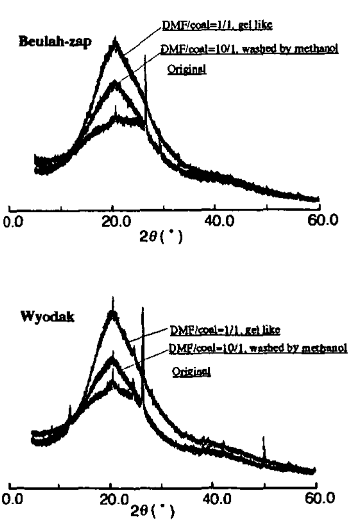

Figure 5 XRD patterns of BZ and WY coals before and after treatment with DMF

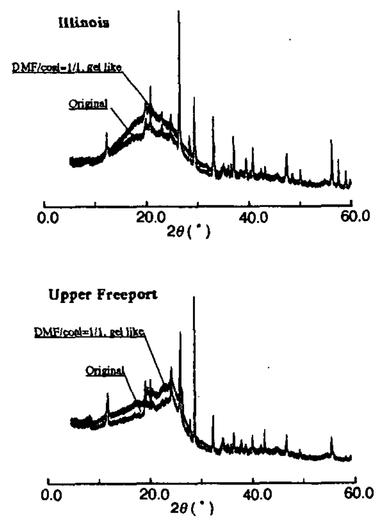

Figure 6 Effct of swelling with DMF on XRD patterns of IL and UF coals